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Pu and Np Sorption onto Manganese(IV) Oxide Minerals

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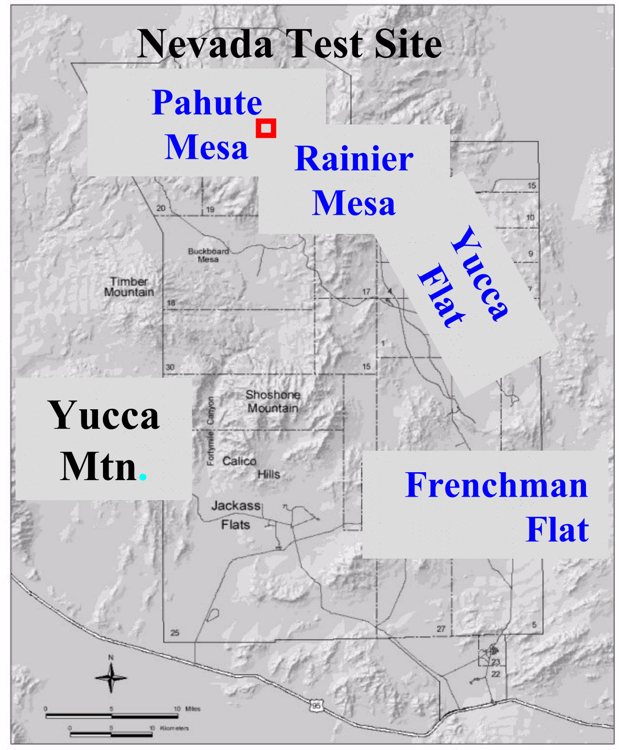
Objectives of this Work

- Manganese oxide minerals are present at Yucca Mountain and are likely to present at NTS as well
- These minerals have high sorption capacity
- Manganese sorption data were not included in the radionuclide transport models
- This results in an over-prediction of radionuclide transport



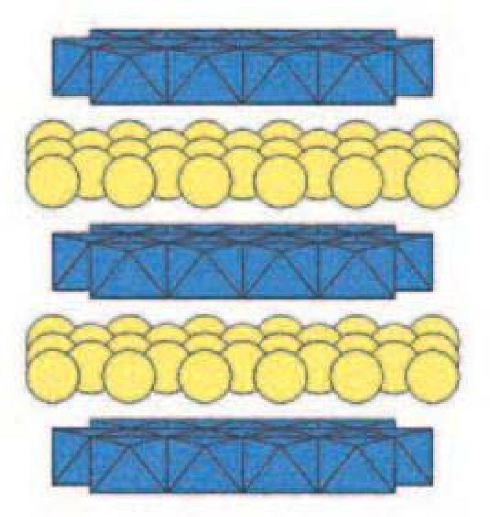
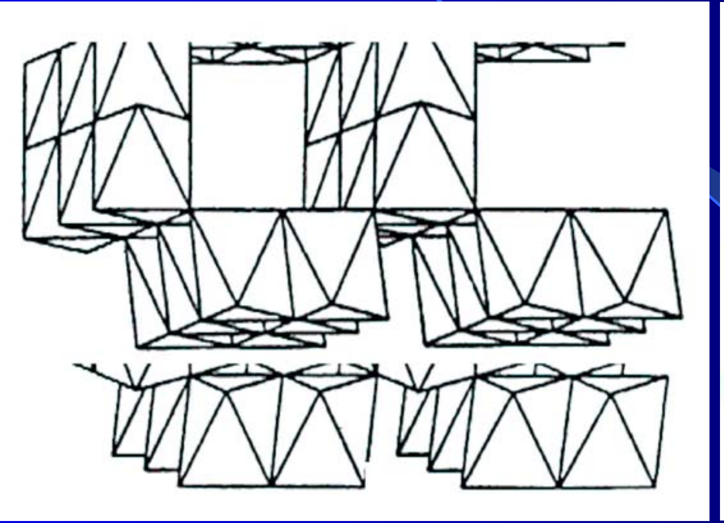
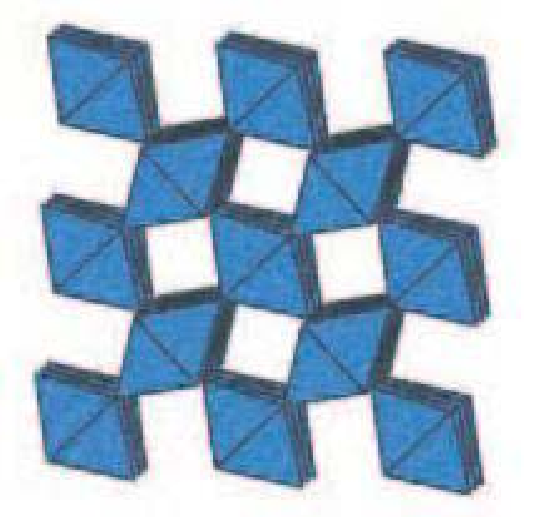
Drellack et al. (1997).

Mineral	Tuff Cone unit Mineral %	Lava Flow Aquifer unit, Mineral %
Chalcedony	24	24
Quartz	5	8
Calcite	3	3
Zeolite	30	35
Clay	11	6
Fe/MnO	20	17
Other	7	7

Experimental Outlines

- Batch sorption Experiments
  - Synthetic minerals birnessite, cryptomelane and pyrolusite
  - K_d vs. pH 3-10,
  - Sorption rate
- Batch desorption experiments
  - sorption reversibility,
  - desorption rate
- Supernatant characterization
  - Solvent extraction
  - Ion Chromatography
  - total carbonate analyses

Manganese(IV) Oxide Minerals

layer structure | tunnel structure | framework structure

Mineral Surface Areas (m^2/g) (BET data)

Birnessite	Cryptomelane	Pyrolusite
41.36 +/- 0.08	11.79 +/- 0.15	2.30 +/- 0.04
54.70 +/- 0.13	10.54 +/- 0.78	

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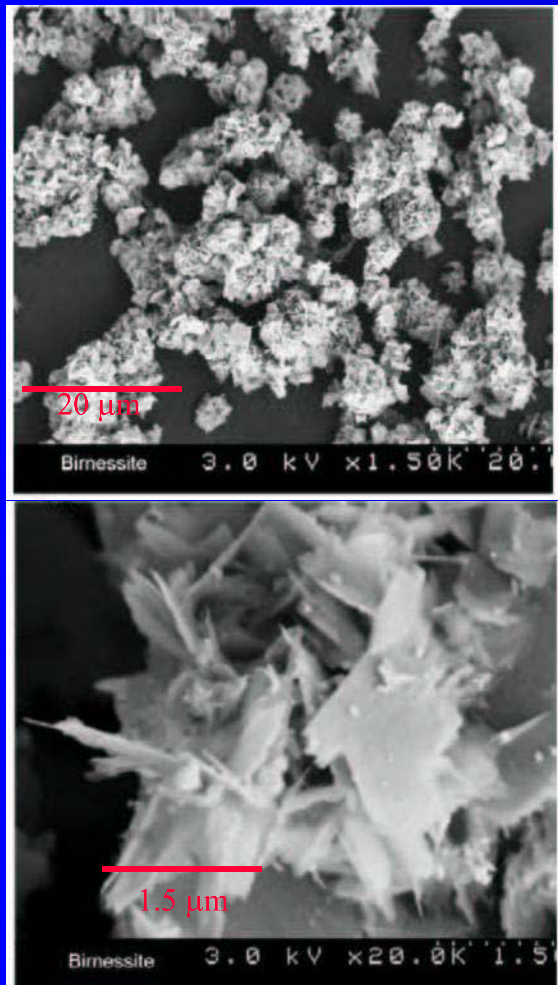
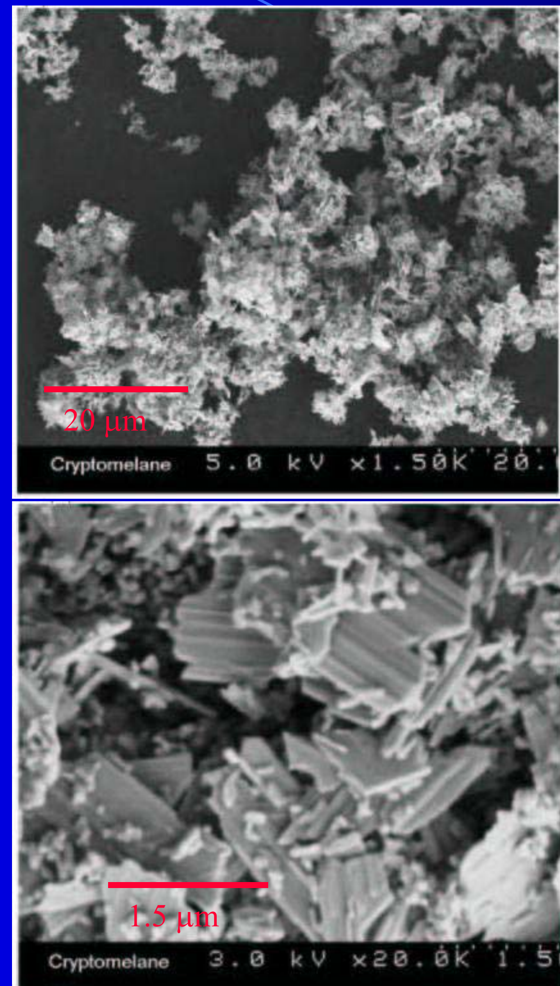
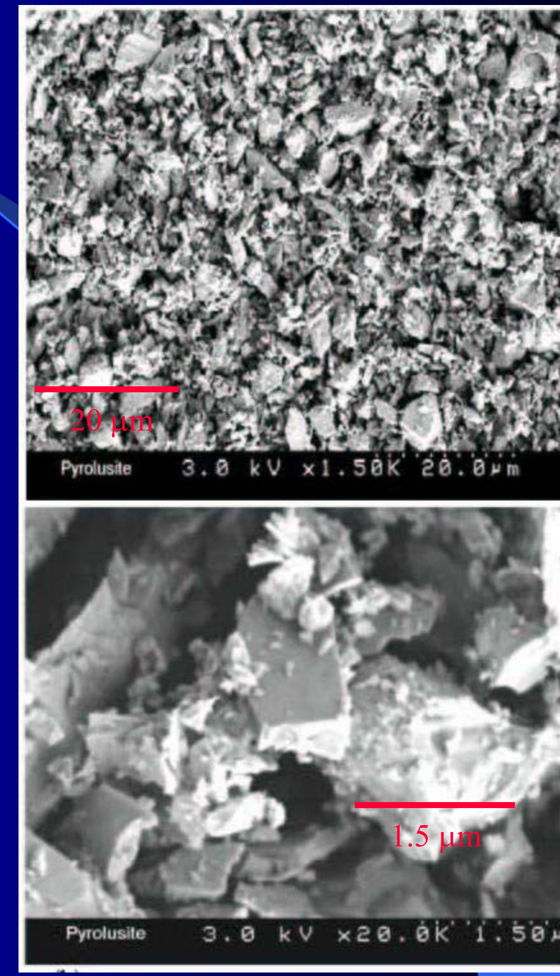
SEM Images of three Manganese Oxides Minerals



Birnessite



Cryptomelane



Pyrolusite

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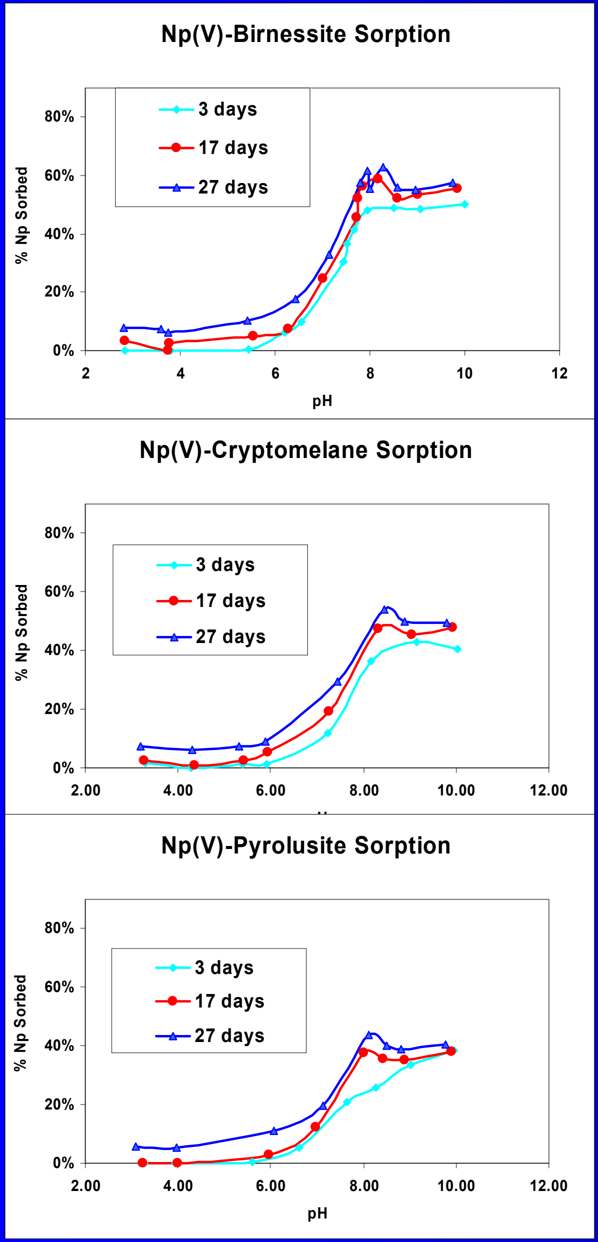
Np(V) sorption onto manganese oxides as a function of time



- Similar sorption behavior at equilibrium.
- The solution pH is a primary factor affecting Np sorption.
- Np-carbonate complexation may reduce the sorption at high pH.
- The sorption rate was fast initially and followed by a slow rate over one month.

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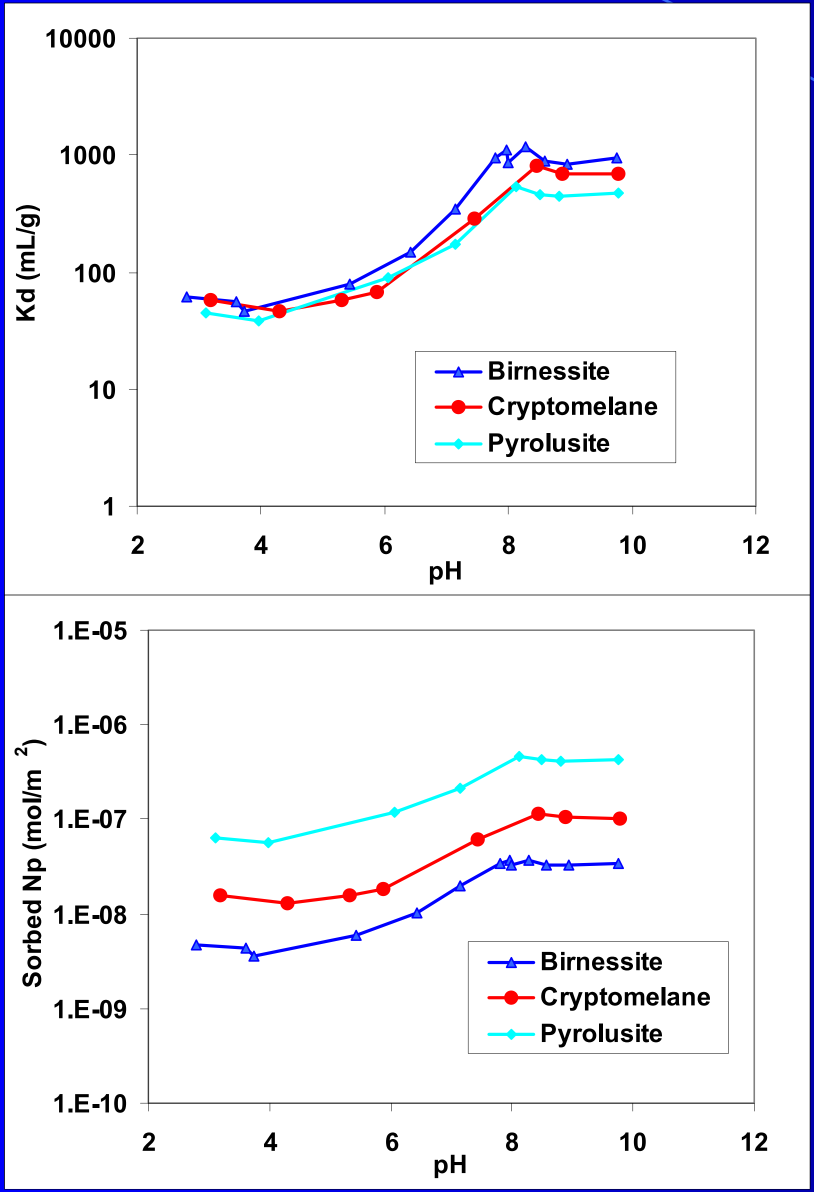
Np(V) Sorption onto manganese oxides



- The K_d values range from <100 at lower pH to >1000 at higher pH.
- Sorption of Np(V) is comparable when examined in terms of %sorbed or K_d values.
- Sorption per unit surface area: Pyrolusite > Cryptomelane > Birnessite.

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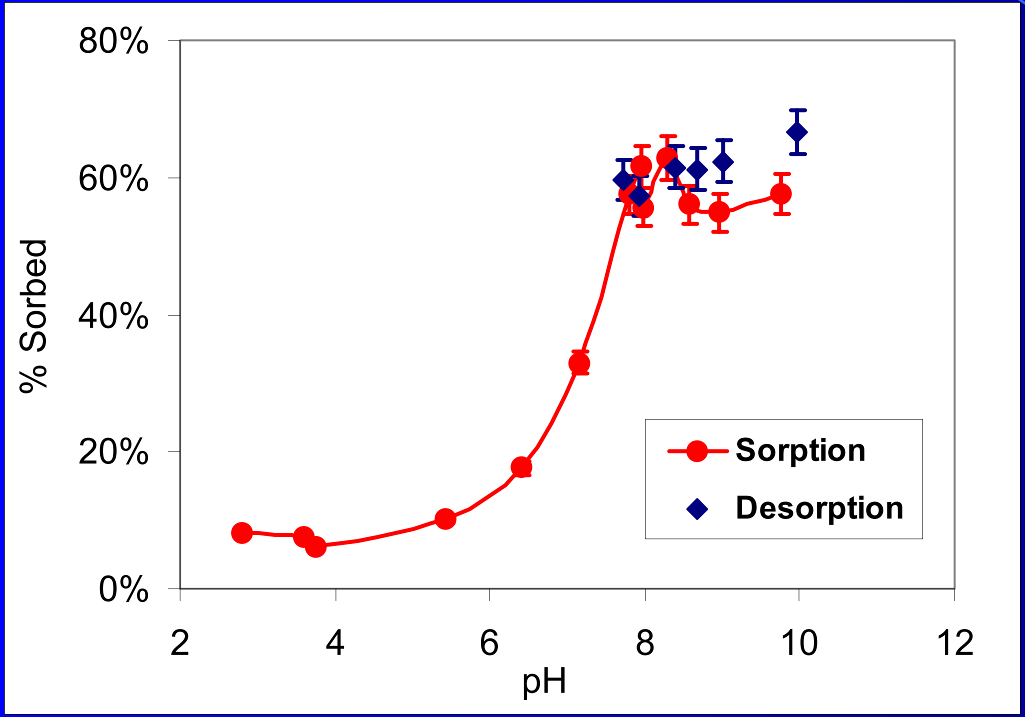
Comparison of Np(V) Sorption / Desorption on Birnessite



- Desorption at range pH 3-6 could not be measured
- Desorption was fast and reversible
- Similar desorption data were observed for cryptomelane and pyrolusite.

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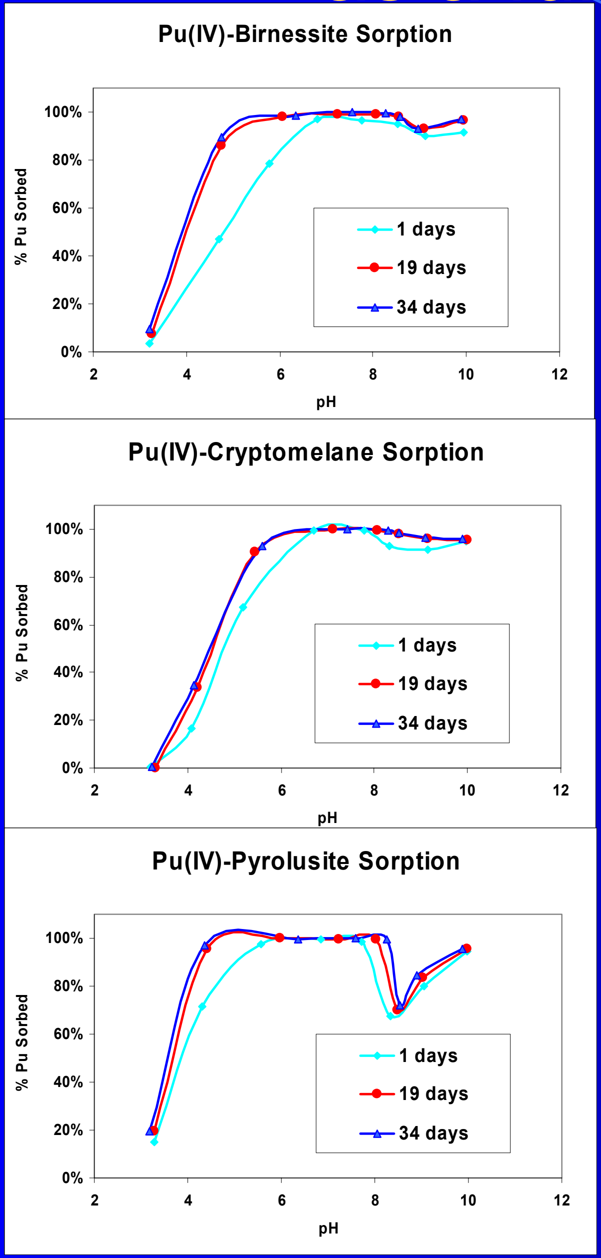
Pu(IV) sorption onto manganese oxides as a function of time



- Similar sorption behavior at equilibrium regardless minerals.
- pH is a primary factor affecting Pu(IV) sorption.
- Pu-carbonate complexation reduces the sorption at high pH.
- Sorption onto all three minerals were very strong in neutral to weak basic solutions.
- The sorption rate was fast for pH > 7, and was relative slow in weak acidic solution.

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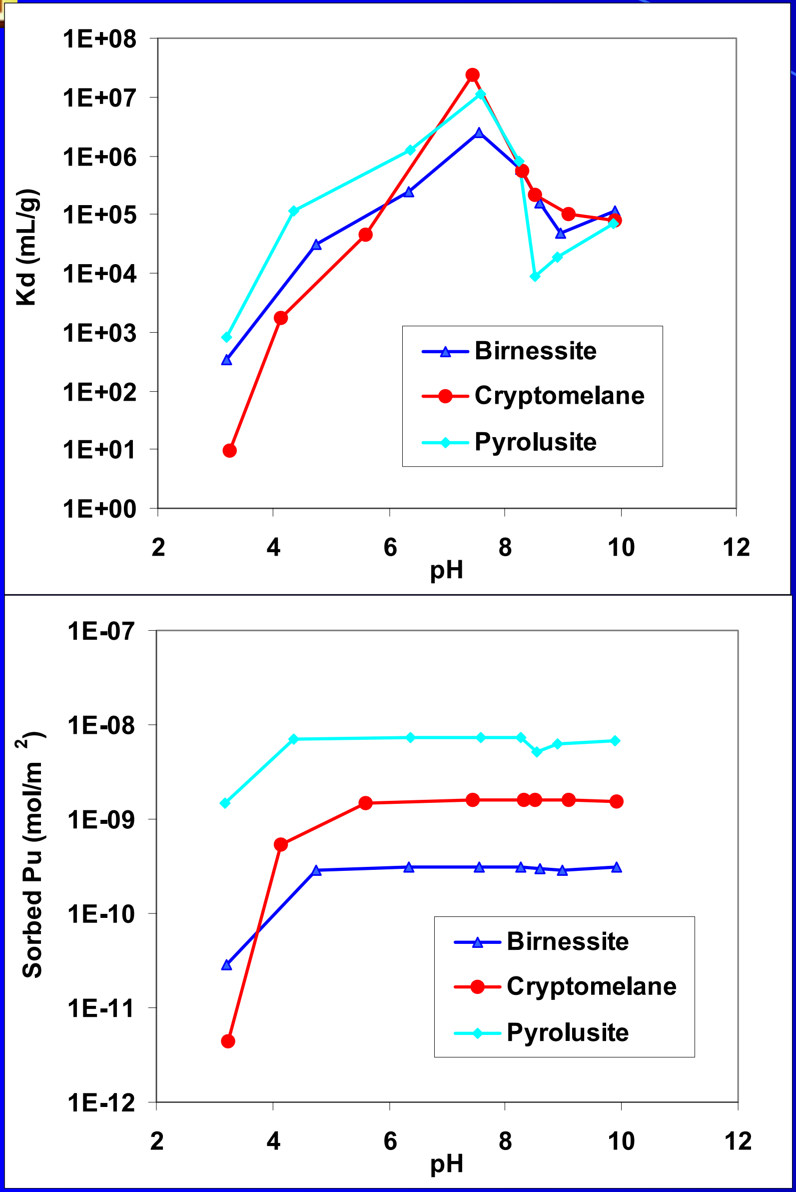
Pu(IV) Sorption onto manganese oxides



- The K_d values change in a wide range from <10 ~ >1E7.
- K_d values unveil the effect of Pu-carbonate complexation at higher pH.
- Sorption per unit surface area: Pyrolusite > Cryptomelane > Birnessite.

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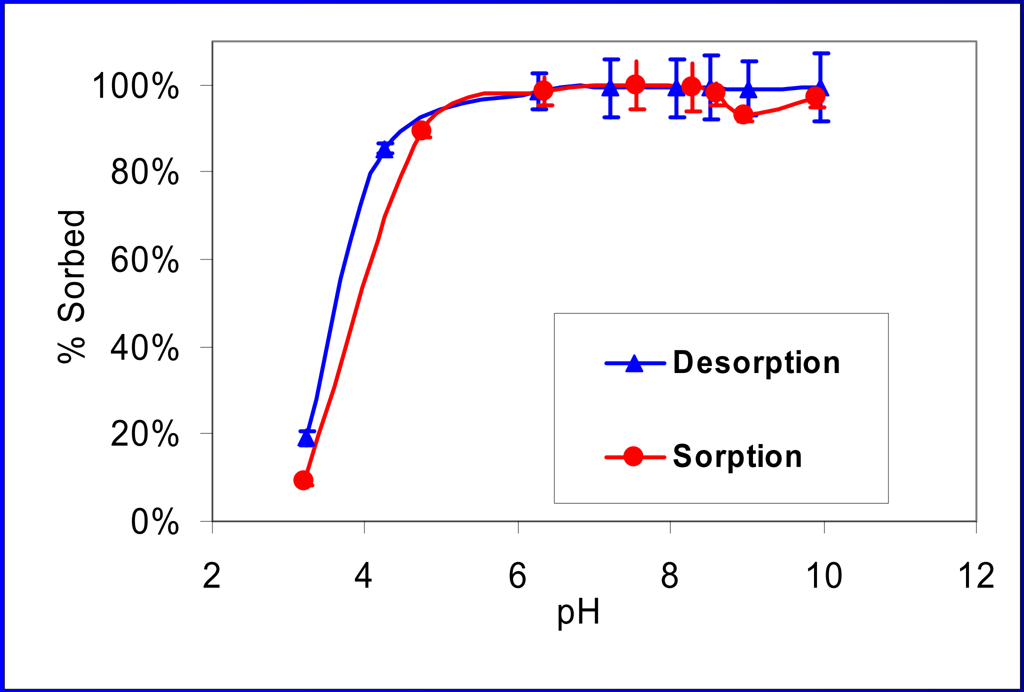
Comparison of Pu(IV) Sorption / Desorption on Birnessite



- Desorption was fast and reversible
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Np Oxidation States in Supernatants from Desorption Experiment

		Percentage of Np oxidation state		
		4+	5+	6+
Birnessite	pH4	1%	92%	7%
	pH7		80%	20%
	pH10		68%	32%
Cryptomelane	pH4	3%	96%	1%
	pH7	1%	97%	2%
	pH10		99%	1%
Pyrolusite	pH4		98%	2%
	pH7**	---	---	---
	pH10		99%	1%

** Data were not available due to very low Np concentration

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Pu Oxidation States in Supernatants from Desorption Experiment

		Pu Oxidation States				colloids
		3+	4+	5+	6+	
Birnessite	pH4		1%	66%	28%	5%
	pH7*	10%	40%	10%	40%	
	pH10	1%	55%	7%	37%	
Cryptomelane	pH4			80%	19%	
	pH7**	---	---	---	---	---
	pH10**	---	---	---	---	---
Pyrolusite	pH4		1%	94%	3%	2%
	pH7**	---	---	---	---	---
	pH10		89%	2%	7%	1%

* Data were associated with large errors

** Data were not available due to very low Pu concentration

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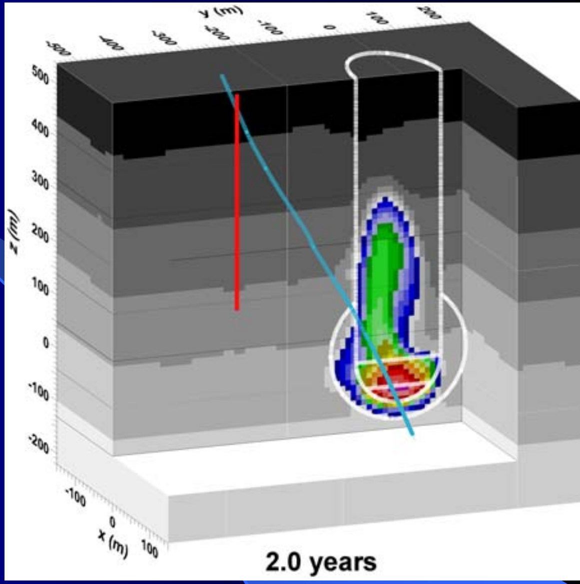
Summary

- Manganese(IV) oxide minerals are good sorbers for Np(V) and very strong sorbers for Pu(IV).
- Sorption of Np(V) and Pu(IV) was fast, reversible, and pH dependent
- On a mass basis, sorption to all three Mn oxides was similar. Base on the BET data, sorption/m^2 followed the order: pyrolusite>cryptomelane>birnessite
- The oxidation states of both Pu and Np appeared to change in the desorption,
- Transport of Pu and Np at NTS locations may be significantly affected by the presence of manganese oxide minerals.
- Future modeling efforts should address the role of Mn oxides in radionuclides transport to more accurately predict their transport



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